Short communication

Field assisted sintering of dense Al-substituted cubic phase Li$_7$La$_3$Zr$_2$O$_{12}$ solid electrolytes

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HIGHLIGHTS

- Pure cubic LLZO is firstly prepared by field assisted sintering technology.
- Cubic LLZO is obtained at lower temperature within a very short sintering time.
- The prepared LLZO has the highest Li ionic conductivity in the present research.
- This work provides a new and very promising method for this material.

ARTICLE INFO

ABSTRACT

High performance lithium ion conducting Li$_7$La$_3$Zr$_2$O$_{12}$ solid electrolytes are prepared for the first time by field assisted sintering technology (FAST). The effect of sintering temperature on the phase compositions, microstructure and Li ionic conductivity is systematically investigated. The results show that pure cubic phase LLZO can be obtained at a range of temperatures from 1100 to 1180 °C for no more than 10 min. For the sample sintered at 1150 °C, a maximum relative density of 99.8% with a total ionic conductivity as high as 5.7×10^{-4} S cm^{-1} are obtained at room temperature. This value is the highest among the present research. Compared with the traditional preparation methods, the current FAST is very promising to obtain high performance LLZO for its advantages of very short sintering time, a single preparation step of reaction-densification processing, and relatively lower sintering temperature.

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1. Introduction

Rechargeable (secondary) all-solid-state lithium batteries are considered to be the next generation high performance power sources and are believed to solve safety issues existing in the current lithium ion batteries with liquid electrolytes [1–3]. A newly developed inorganic solid state electrolyte material, Li$_7$La$_3$Zr$_2$O$_{12}$ (LLZO) with garnet structure has attracted increasing attention over the past few years due to its superior properties, such as chemical stability against reactions with lithium metal electrode, high lithium ion conductivity, good thermal and environmental benignity [4–11]. The LLZO has two phases: cubic phase and tetragonal phase [12]. Reports have estimated theoretical bulk Li-ion conductivity for cubic phase of $\sim 10^{-3}$ S cm^{-1} available for application, compared to

$\sim 10^{-6}$ S cm^{-1} [6] for the tetragonal phase, which may not be applied. However, it is difficult to obtain the cubic phase LLZO. Firstly, lithium is very easy to be lost which results in the formation of the pyrochlore phase La$_2$Zr$_2$O$_7$. Secondly, the cubic phase was reported to be obtained in a narrow sintering temperature range between 1150 and 1230 °C [5]. Thirdly, the pure cubic phase was unstable at room temperature. Several groups [13–15] have reported that a small concentration of Al is necessary for the stability of the cubic phase calcined at high temperature. Geiger et al. [13] studied the material by X-ray powder diffraction at different temperatures between 25 °C and 200 °C. They found that LLZO with Al are cubic crystals with space group Ia-3d at all temperatures, while LLZO without Al is tetragonal at room temperature and undergoes a phase transition to a cubic phase between 100 °C and 150 °C. Rangasamy et al. [14] investigated the effect of Al and Li concentration on the formation of cubic garnet of LLZO and found that at least 0.204 moles of Al is required to stabilize the cubic phase.

In previous studies, the solid state reaction methods were often used to prepare solid electrolyte LLZO [1–5,8]. Murugan et al. [4]

firstly succeeded in synthesizing cubic LLZO by sintering at a high temperature of 1230 °C for 36 h and got a high total (bulk + grain boundary) ionic conductivity of 3×10^{-4} S cm^{-1}. In the conventional solid state reaction method, repeated heat treatments at high temperatures and intermittent grinding are necessary to ensure that the oxide precursors react thoroughly. Long sintering time causes high cost and low efficiency for this preparation. Moreover, the long sintering times and high sintering temperature often result in impurity phases due to lithium loss at high temperature and Al incorporation, particularly if alumina crucible are used. Attempts were made later to prepare nano LLZO powders by using solution based methods [6,9–12]. The nano LLZO powders have good sinterability and cubic phase LLZO had been produced at low temperature of 700 °C [9,10]. However, the obtained cubic phase LLZO pellet often shows low total ionic conductivity, such as, the resulting ionic conductivity prepared by Xie et al. [9] is 2.85×10^{-6} S cm^{-1}. The possible reason is that those powders synthesized by solution based methods contain impurities and the pellets sintered at low temperatures have porous structures.

Field assisted sintering technology (FAST) is a combination of a uniaxial pressing process and a direct passing of electric DC current through the graphite tool to sinter the material, if the powder is not electrically conductive. The production of Joule heat within tool enables the densification of various materials with higher heating rates and shorter dwell times [16]. It is expected that the high sintering rates of FAST for preparation of LLZO can extremely reduce the loss of Li and the pressure during the sintering can densify the sample at the same time. Moreover, the chemical reaction between the raw materials to synthesis LLZO and the sintering densification of the pellets are both accomplished in one step during the field assisted sintering technology without any other heat treatment and intermittent grinding.

In this work, FAST is applied for the first time to fabricate the lithium ion conducting LLZO. The effect of sintering temperature on the phase compositions, microstructure and Li ionic conductivity of the sintered samples is comprehensively investigated.

2. Experimental procedures

High purity Li$_2$O (purity of 99.99%, particle size of ~10 μm, produced by Aladdin), La$_2$O$_3$ (purity of 99.99%, ~10 μm, produced by Sinopharm Chemical Reagent Co., Ltd., China), ZrO$_2$ (99.9%, ~5 μm, produced by Guangdong Orient Zirconic Ind. Sci. & Tech. Co., Ltd., China) powders were employed, the molar ratio among Li, La, and Zr was controlled as 7:3:2. 1.5 wt.% γ − Al$_2$O$_3$ (99%, 20 nm, produced by Aladdin) was added as additive.

Firstly, the powders were ball milled using zirconia balls in 2 − propanol for about 12 h and then the powders were dried in vacuum oven at 80 °C for 6 h. Secondly, powders were loosely filled into the graphite die and then it was put into the FAST system. FAST consolidation was conducted with a plasma activated sintering system (ED − PASIII, Elenix Ltd., Japan). Before the sintering, there was an activation step running for 30 s with a pulse current of 30 V/10 A. Sintering process was performed at the temperature range of 900 °C to 1230 °C under a constant uniaxial pressure of 10 MPa with a holding time of 3 min. The subsequent heating rate was set as 300 °C/min. Temperature measurement and control were conducted using pyrometer through the hole of the die. Ar was filled into the system as protect gas to balance the pressure in order to prevent the loss of lithium. After the dwell, sample was cooled down to room temperature naturally.

The phase structure of the LLZO ceramics was characterized by X-ray diffraction (XRD, Rigaku Ultima III) with Cu Kα radiation over the range of 10–90° (2θ). The microstructure of the ceramics was observed by field-emission scanning electron microscopy (FESEM, FEI-Quanta-250). The density of the ceramics was measured by the Archimedes' method. The Li ionic conductivity was measured using an electrochemical workstation (Autolab PGSTAT 30) in the frequency range from 10 Hz to 10 MHz at room temperature and an impedance analyzer (Agilent E4980A) in the frequency range from 20 Hz to 2 MHz at elevated temperature range of 50–300 °C. A thin film of Au was sputtered on both sides of pellet for the experiments blocking electrodes. Impedances were determined from the intercepts of the relevant capacitive arcs at the real axes in the Nyquist plots and conductivities were calculated using the following equation:

$$\sigma = (1/Z)(L/A) \tag{1}$$

where σ is the ionic conductivity, Z is the impedance, L is the pellet thickness, and A is the pellet area. Typical dimensions of the pellets were 1.5–2.0 mm in thickness, 10 mm in diameter.

3. Results and discussion

The XRD patterns of the samples sintered by FAST at various temperatures from 900 °C to 1230 °C are shown in Fig. 1. The pure cubic LLZO pattern at the bottom is simulated based on structural parameters found in Ref. [13]. It is seen that cubic phase LLZO appears at a low temperature of 900 °C, but with a few peaks of La$_2$Zr$_2$O$_7$ phase simultaneously. As the temperature rises up to 1000 °C, the impurity phase of La$_2$Zr$_2$O$_7$ disappears. However, some peaks obviously become broad and have shoulders, which are diffracted from tetragonal phase. Therefore, the pellet is a mixture of cubic and tetragonal phases. For the sample sintered in the temperature range of 1100–1180 °C, the peaks are sharp without any shoulders, revealing the formation of a well crystallinity and high purity of the cubic phase LLZO. Thus, LLZO might undergo a phase transition in the temperature range of 1000–1100 °C. With
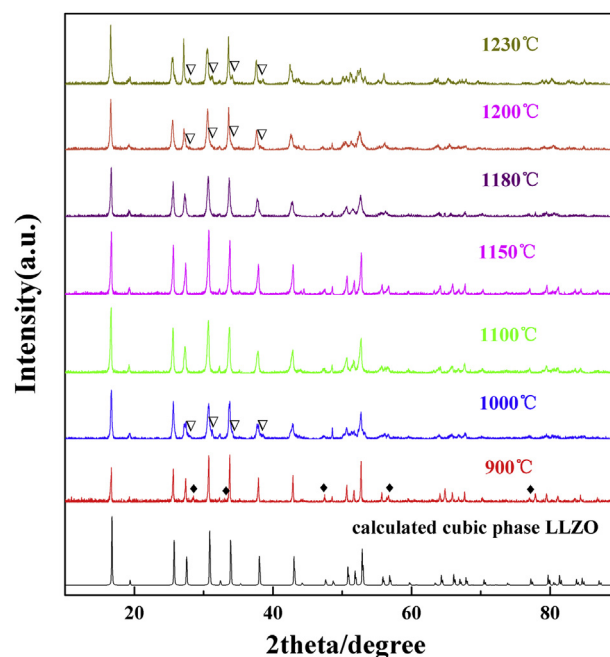

Fig. 1. XRD spectra of Li$_7$La$_3$Zr$_2$O$_{12}$ samples sintered by FAST at temperature from 900 °C to 1230 °C, the pattern in the bottom is simulated based on the structure of cubic LLZO from Ref. [13]. (♦ La$_2$Zr$_2$O$_7$; ∇ Some characteristic peaks of tetragonal phase).

increasing the temperature to 1200 °C, the peaks become broad again which is similar to that of 1000 °C, suggesting the emergence of mixed phases of tetragonal and cubic. With the temperature further increased to 1230 °C, part of the single Bragg peak splits into two diffraction peaks which derive from the tetragonal structure of LLZO. From the above analysis it is apparent that cubic phase can be obtained in a sintering temperature range between 1100 °C and 1180 °C. The temperature for obtaining the cubic LLZO phase is relatively lower than that of the conventional solid state reaction methods (1230 °C [4]). This could be caused by the field effect which has cleaned up the surface adsorbates thus reducing the activation energy of sintering.

In our experiment, Li is not excess added which is different from the conventional methods (currently excess 10%) to compensate for the loss of Li, but cubic phase LLZO is still obtained which means Li did not loss too much to affect the formation of the target product. As it is reported by Rangasamy [14], single cubic LLZO exists when the Li content is between 5.63 and 6.24 moles with the Al concentration of 0.24 mol (1.5 wt. %). This indicates that the loss of Li during the FAST process is very limited. The limited loss of Li is mainly because the total sintering time by FAST is no more than 10 min, which is comparatively very short.

Fig. 2 shows the SEM micrographs of the cross sections of the samples sintered at various temperatures. For the pellet sintered at low temperature of 1000 °C (Fig. 2(a)), the particles have not fully grown with a non-uniform grain size in the range of 1–7 μm. The contact between the grains is insufficient, a few voids are observed. As the temperature rises up to 1100 °C (Fig. 2(b)), the grains become regular and grows bigger than that of 1000 °C, part of the fracture is transgranular. In contrast to these two samples, the particles sintered at the temperature of 1150 °C and 1200 °C (Fig. 2(c)–(d)) contact tightly each other with no voids, the fracture is almost transgranular with an average grain size of about 10 μm.
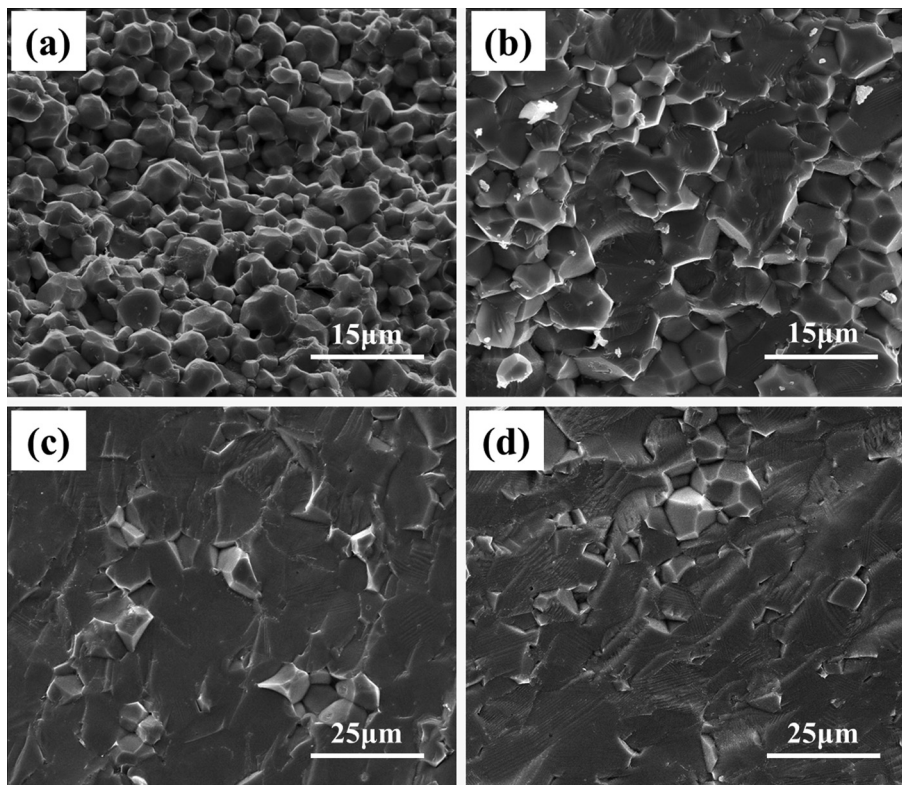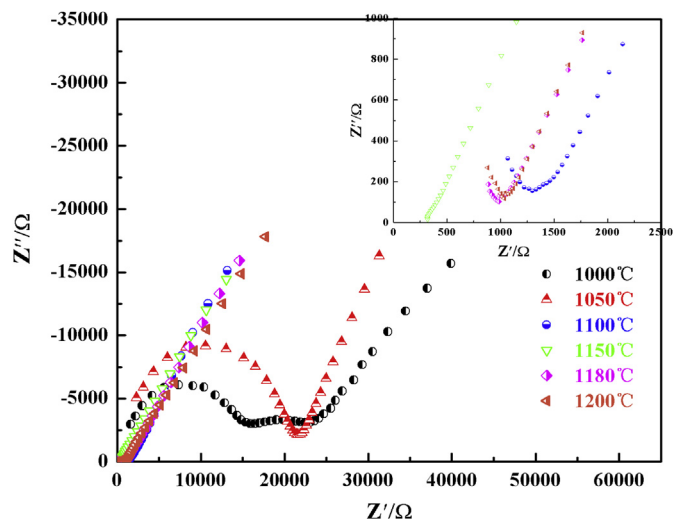

Fig. 3. Nyquist plots (frequency range: 10 Hz–10 MHz) of the samples sintered 1000–1200 °C measured at room temperature.

Typical Nyquist plots of LLZO pellets sintered at various temperatures which are measured at room temperature are shown in Fig. 3. The appearance of the tail at low frequencies arises from the ionic blocking electrode, indicating that the investigated material is ionically conducting in nature [4]. For the ceramics sintered at 1000 °C, the impedance plot could be well resolved into bulk, grain boundary, and electrode resistances. At the sintering temperature higher than 1100 °C, no clear semicircles at high frequencies are observed. This is in good agreement with the results of Kotobuki et al. [18], who suggested that the lack of clear semicircle at the high

Fig. 2. SEM micrographs of the cross sections of the samples sintered at (a)1000 °C, (b)1100 °C, (c)1150 °C and (d)1200 °C.

Table 1
Mass density, relative density and 25 °C Li$^+$ conductivity of LLZO samples sintered at different temperatures.

Temperature	1000 °C	1050 °C	1100 °C	1150 °C	1180 °C	1200 °C
Phase compositions	M[a]	M	C[b]	C	C	M
Mass density (g cm^{-3})	4.33	4.51	4.99	5.09	5.04	5.02
Relative density (%)	n/a	n/a	97.9	99.8	98.9	n/a
25 °C Li$^+$ conductivity (S cm^{-1})	1.1×10^{-5}	1.2×10^{-5}	1.6×10^{-4}	5.7×10^{-4}	4.8×10^{-4}	1.8×10^{-4}

[a] M stands for a mixture phase of cubic and tetragonal.
[b] C stands for cubic phase.

frequencies in their impedance plots implied that grain boundary impedance is negligible compared to the lattice impedance and Kumazaki et al. [3] who suggested that the lack of a clear semicircle in the highest conductivity sample was a result that the grain boundary resistance was almost completely removed in this sample. In our experiments, it is considered that the grains growth is directly related with the increase of the sintering temperature, which reduces the number of grain boundaries thus resulting in the lack of clear semicircle.

Using the high frequency intercept on the Z′ axis and the sample dimensions yields total (bulk + grain boundary) ionic conductivity values. Table 1 summarizes the density, relative density and lithium ion conductivity of the LLZO pellets sintered at various temperatures. As shown in Table 1, the pellets sintered at 1100 °C, 1150 °C and 1180 °C are all cubic phase, while the other pellets show mixed phases (as discussed in the XRD results). Because the content of the tetragonal phase is unknown in these pellets with mixed phases, the relative density of these samples cannot be calculated. The sample sintered at 1150 °C reaches the maximum relative density of 99.8% and has the highest ionic conductivity of 5.7×10^{-4} S cm^{-1} compared with that of 1100 °C and 1180 °C. This indicates the density is a key factor for the Li ionic conductivity of cubic LLZO. It is noted that the phase purity of LLZO is also critical for the Li ionic conductivity. As can be seen in Table 1, the Li ionic conductivity of the pellet sintered at 1200 °C is lower than that of 1180 °C, which could due to the presence of a small amount of the tetragonal phase. On one hand, as can be inferred from the XRD pattern, the content of tetragonal phase of the sample sintered at 1200 °C is very low. On the other hand, the theoretical density of pure cubic LLZO (5.098 g cm^{-3} [7]) has little difference with that of tetragonal LLZO (5.106 g cm^{-3} [19]). Thus, the relative density of the sample sintered at 1200 °C is considered almost identical to that of 1800 °C. Herein, it is considered that the deterioration of the ionic conductivity of 1200 °C is mainly caused by phase impurity of tetragonal

phase. So we conclude that both the relative density and the phase purity of cubic LLZO have a significant effect on the Li ionic conductivity.

Fig. 4(a) shows the Nyquist plot of the impedance spectrum measured at temperatures between 50 °C and 300 °C for the cubic phase LLZO sintered at 1150 °C. The temperature dependence of the total conductivity (Arrhenius plot) is shown in Fig. 4(b) and can be expressed by the Arrhenius equation [10]:

$$\sigma = \frac{A}{T} \exp\left(\frac{-E_a}{k_B T}\right) \tag{2}$$

where σ is the ionic conductivity, T the absolute temperature, A the pre-exponential constant, k_B the Boltzmann constant and E_a is the activation energy for the ionic conductivity. From Fig. 4(b), the activation energy determined from the slope of the log (σT) versus $1/T$ plot for the total conductivity in the temperature range of 50–300 °C is 0.30 eV. This activation energy value is exactly the same value as determined by Murugan et al. [4] using solid state reaction method.

The properties of cubic LLZO ceramic prepared by FAST in this work and by other methods are listed in Table 2. The cubic phase LLZO prepared by FAST has the highest total ionic conductivity among the results of the present research. The high performance might attributes to two aspects. Firstly, the high purity of cubic LLZO phase. FAST has a very short sintering time and relative lower sintering temperature, both can efficiently reduce the loss of Li compared with the long synthesis process in the conventional solid state sintering method. It also has just one step heat treatment process including both the reaction and densification process which effectively avoids the introduction of impurities. In the conventional solid state sintering method, several steps of heat treatment processes are often been conducted which can easily bring some impurities into the samples. Secondly, the high density
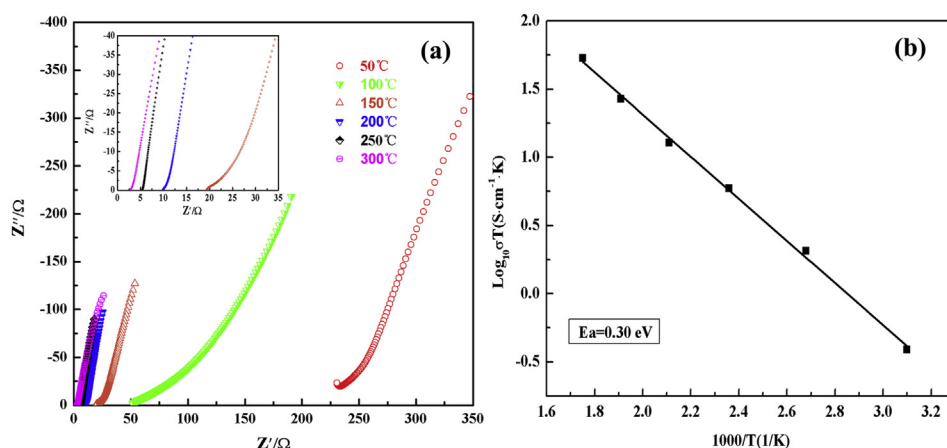
Fig. 4. (a) Nyquist plots (frequency range: 20 Hz–2 MHz) for the total (bulk + grain boundary) ion conductivity measured at temperatures between 50 °C and 300 °C of LLZO samples sintered at 1150 °C, and (b) Arrhenius plot for total conductivity of cubic LLZO prepared by FAST.

Table 2
Comparison of properties of cubic LLZO ceramics fabricated by several methods.

Methods	Properties		
	Sintering conditions	Relative density/%	Total ionic conductivity/S cm^{-1}
Solid state reaction [1], [4], [5]	1230 °C − 36 h [5]	96.0 [5]	3.6 × 10^{-4a} [5]
Solution based methods [6], [9], [11]	1200 °C − 6 h [11]	86.3 [11]	2.0 × 10^{-4a} [11]
This work	1150 °C − 10 min	99.8	5.7 × 10^{-4}

[a] the best value found among the papers using that method.

of cubic LLZO phase. The applied pressure during FAST process is essential for the densification of the LLZO ceramics which has the advantage over the pressureless sintering method. The dense LLZO ceramics elevates the total ionic conductivity and prevents the penetration of lithium dendrites through the pores during cycling, which may lead to an electrical short or fracturing of the sample. The above advantages indicate that this sintering technology is a particularly efficient method for preparing high Li ionic conductivity cubic phase LLZO solid electrolytes.

4. Conclusions

High performance lithium ion conducting Li$_7$La$_3$Zr$_2$O$_{12}$ solid electrolytes with cubic phase have been successfully prepared for the first time by a one-step FAST method. The experiment results show that pure cubic LLZO phase can be obtained in the temperature range of 1100−1180 °C for a very short sintering time of no more than 10 min. The particles grow up and contact tightly with the rising of temperature, for the sample sintered at temperature of 1150 °C and 1200 °C, the fracture is almost transgranular with an average grain size of about 10 μm. The sample sintered at 1150 °C has a maximum relative density value of 99.8% and the highest ionic conductivity value of about 5.7 × 10^{-4} S cm^{-1} which is the best value found in the present reports. The activation energy of the sample is 0.3 eV in the temperature range of 50−300 °C. Both the relative density and the phase purity of the cubic LLZO have a significant effect on the Li ionic conductivity. By comparison, FAST shows great advantages for synthesizing this material including

very short sintering time, relative lower sintering temperature, one step heat treatment process and higher performance of sintered LLZO ceramics over other reported methods. The present work provides a new and very promising method for the preparation of high performance LLZO solid electrolytes.

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